Hexadimethrine-montmorillonite nanocomposite: characterization and application as a pesticide adsorbent

B. Gámiz*, M.C. Hermosín, J. Cornejo, R. Celis

Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC, Avenida Reina Mercedes 10, P.O. Box 1052, 41080 Sevilla, Spain

*Corresponding author:

Dr. Beatriz Gámiz

Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC

Avenida Reina Mercedes 10, P.O. Box 1052

41080 Sevilla

SPAIN

Phone: +34 954624711

Fax: +34 954624002

E-mail: bgamiz@irnase.csic.es

Abstract

The goal of this work was to prepare and characterize a novel functional material by the modification of SAz-1 montmorillonite with the cationic polymer hexadimethrine (SA-HEXAD), and to explore the potential use of this nanocomposite as a pesticide adsorbent. Comparative preparation and characterization with the well-known hexadecyltrimethylammonium-modified SAz-1 montmorillonite (SA-HDTMA) was also assessed. The characterization was performed by elemental analysis, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), physisorption of N_2, scanning electron microscopy (SEM) and Z potential measurements. The characterization and adsorption experiments showed that the extent of pesticide adsorption was markedly subjected to the structure and features of the surface of each organo-clay and also to the nature of the considered pesticide. SA-HEXAD displayed a high affinity for anionic pesticides which, presumably, were adsorbed by electrostatic attraction on positively-charged ammonium groups of the polymer not directly interacting with the clay. In contrast, SA-HDTMA displayed great adsorption of both uncharged and anionic pesticides with predominance of hydrophobic interactions. This work provided information about the surface properties of a new organic-inorganic nanohybrid material, SA-HEXAD, and its potential as an adsorbent for the removal of anionic organic pollutants from aqueous solutions.

Keywords: Adsorption; Functionalization; Nanostructured materials; Nanohybrids; Polymers

1. Introduction

Clay minerals have attracted attention over the last decades for being naturally occurring and versatile materials. The importance of these materials lies on their peculiar properties such as small particle size, swelling capacity, anisotropic shape, reactive surfaces, and high cation exchange capacity (CEC) [1,2]. As a consequence, a vast number of applications have been projected for clay minerals; among others, their use as adsorbents of pollutants in order to reduce their environmental impact [3]. The interest in clay minerals has grown as the development of nanoscience and nanotechnology has progressed, due to their nano-sized layers and interlayer space [4–6].

Expandable clay minerals (i.e., smectites) have a marked hydrophilic character caused by the strong hydration of the inorganic counter ions present in the interlayer space. Indeed, they are rarely good adsorbents for hydrophobic organic compounds [7–10]. Nevertheless, the modification of the nature of the clay mineral surface from hydrophilic to hydrophobic through ion-exchange reactions replacing the inorganic cation with an organic cation can dramatically alter the affinity of smectites toward hydrophobic organic compounds. The resulting so-called organo-clays have been extensively proposed as adsorbents for poorly water soluble, highly hydrophobic compounds [3,11–15].

Alkylammonium-exchanged smectites have been the most common organo-clays proposed for adsorption of pesticides [3,16]. Celis et al. [17] found that the adsorption of the neutral fungicide triadimefon reached values higher than 90% after the modification of SAz-1 montmorillonite with hexadecyltrimethylammonium (HDTMA) monomeric cations, and a similar behavior was observed for neutral phenylureas pesticides[18,19]. Noticeable increases in adsorption of SAz-1 after its modification with HDTMA cations have also been reported for acidic pesticides, such as 2,4-D [13], imazamox [20], bentazone and dicamba [21], picloram [22] and MCPA [23,24]. However, several studies have pointed out that quaternary

alkylammonium ions such as HDTMA may have undesirable toxicological properties which may limit their usefulness for environmental applications. Several studies reported antimicrobial properties for this type of organo-clays, which can thus be toxic for natural xenobiotic degraders and hinder natural attenuation of pollutants in the environment [25,26]. Hence, new strategies to circumvent the limitations of traditional alkylammonium-modified clay minerals are needed. Alternative methods involve, for instance, preparation of clay-organic nanohybrid or nanocomposite materials using more friendly organic cations, capable of reducing the impact of the adsorbent once it is incorporated into natural environments for practical applications [18,24,27–30].

It is well-known that the leading mechanism in the adsorption of organic solutes by organo-clays will depend, for a given clay mineral, on the properties of the organic modifier and those of the selected solute [3,6]. The principal mechanism for the adsorption of organic pollutants on the traditional HDTMA-modified Arizona montmorillonite (SA-HDTMA) is the solute partitioning into the paraffinic-like organic phase formed by the vertical arrangement of HDTMA cations in the interlayer space of the clay mineral, which provides an excellent medium for the adsorption of hydrophobic organic compounds [11,31–33]. In the interaction of SA-HDTMA with anionic pesticides, including those of the phenoxyacetic group, polar interactions have also been proposed, in addition to hydrophobic interactions, as long as free polar space exists between alkylammonium groups in the organo-clay interlayer to host the pesticide [13,20,34–36].

In a preceding work, we found that the modification of SAz-1 Arizona montmorillonite with the cationic polymer hexadimethrine rendered a nanocomposite which displayed an affinity for the anionic pesticide MCPA comparable to that of the traditional SA-HDTMA organo-clay [24]. Given that the full potential of clay-organic nanohybrid materials has not been achieved due to limited understanding of the interaction mechanisms between different target

compounds and the clay matrix [16], we aimed in this work at getting further insight into the interaction mechanisms governing the adsorption of a number of structurally different pesticides, as representatives of widely spread pollutants in the environment, and the novel hexadimethrine-montmorillonite (SA-HEXAD) nanohybrid material, comparing its behavior with that of the well-known SA-HDTMA organo-clay. For the purpose of this work, HDTMA and HEXAD are excellent models of monomeric versus polymeric alkylammonium-type modifiers lacking additional specific functional groups for the adsorption of pesticides. The specific objectives of this work were: i) a detailed and comparative characterization of the SA-HEXAD and SA-HDTMA systems, and ii) a comparative assessment of the adsorption of a suite of structurally different pesticides by SA-HEXAD and SA-HDTMA, to get further insight into the mechanisms governing the affinity of these nanohybrids for selected pesticides. The information reported in this paper should be useful for the implementation of the assayed materials in specific applications, such as the removal of pesticides from contaminated water, their immobilization in soil, or the preparation of slow release formulations.

2. Experimental

2.1 Montmorillonite, organic cations and pesticides

The reference Ca-rich Arizona montmorillonite (SAz-1) from the Source Clays Repository of the Clay Minerals Society (Purdue University, West Lafayette, IN), with CEC equal to 1200 mmol/kg, was used for the preparation of the organo-clays. The properties of SAz-1 montmorillonite have been reported elsewhere [37].

Hexadimethrine (HEXAD) bromide (purity > 95%) and hexadecyltrimethylammonium (HDTMA) chloride (purity ≥ 98%) (Fig. S1) were purchased from Sigma-Aldrich. Hexadimethrine is an agglutinant blood cell polycation employed as heparin-neutralizing in

pharmaceutical industry [38]. Hexadecyltrimethylammonium is a cationic surfactant which has been widely used, among other applications, for the preparation of organo-clays [3,39].

Selected analytical-grade (purity > 99.9%) pesticides (fluometuron, diuron, terbuthylazine, simazine, mecoprop, MCPA, and clopyralid) supplied by Sigma-Aldrich were used for adsorption experiments. The structures of the pesticides are shown in Fig. 1.

2.2. Preparation of SA-HEXAD and SA-HDTMA nanohybrids

Preparation of SA-HEXAD and SA-HDTMA was accomplished through a cation exchange reaction, following the procedures described in Celis et al. [24,40]. Briefly, raw SAz-1 was treated with an aqueous solution containing an amount of organic cation (HEXAD or HDTMA) equivalent to 100% of the cation exchange capacity (CEC) of the clay mineral. The suspensions were shaken for 24 h, centrifuged, and the resulting solid was washed three times with deionized water, freeze-dried, and stored at room temperature until used.

2.3. Characterization of the unmodified and modified-montmorillonite samples

The C and N contents of the unmodified and modified-montmorillonites samples were determined by the combustion method using a Perkin-Elmer, model 1106 elemental analyzer (Perkin-Elmer Corp., Norwalk, CT). The basal spacings (d_{001}) of oriented clay specimens were determined with a Siemens D-5000 diffractometer (Siemens, Stuttgart) with CuK_{α} radiation. A Jasco FT/IR 6300 spectrometer (Jasco Europe s.r.l.) provided with a diffuse reflectance accessory was employed to record the Fourier-transform infrared (FTIR) spectra. Physisorption of N_2 at 77 K, using a Carlo Erba Sorptomatic 1900 (Fisons Instruments, Milan) gas adsorption analyzer, was used to obtain the specific surface area (SSA) by applying the BET method. Zeta potential distribution curves for SAz-1, SA-HEXAD and SA-HDTMA suspensions (1.4 mg mL^{-1}) were measured with a Zetasizer Nano ZS equipment (Malvern

Instrument). Z potential (ξ) values were obtained at the pH of the suspension, previously dipped into an ultra-sound bath to disperse aggregates before analysis. Finally, scanning electron microscopy (SEM) was used to get insight into the morphology of the samples using a Hitachi S5200 microscope.

2.4. Adsorption studies

Adsorption experiments were conducted to determine the performance of SA-HEXAD as an adsorbent of a number of structurally different pesticides and to compare its behavior with that of SA-HDTMA, particularly with regard to different adsorption mechanisms possibly involved.

2.4.1. Preliminary adsorption study

A preliminary adsorption study with seven different pesticides (Fig. 1) was performed at a single initial pesticide concentration of 1 mg L^{-1}, using the batch equilibration technique. Triplicate 20 mg of SAz-1, SA-HEXAD or SA-HDTMA were placed in glass centrifuge tubes lined with screw caps. Subsequently, the clay samples were equilibrated with 8 mL of separate aqueous solutions of each pesticide with an initial concentration Ci= 1 mg L^{-1} by shaking at 20 ± 2°C for 24 h. After equilibration, the suspensions were centrifuged and 4 mL of the supernatant solution was removed, filtered, and analyzed by high performance liquid chromatography (HPLC) to determine the pesticide equilibrium concentration in solution, Ce (mg L^{-1}). Triplicate initial pesticide solutions of pesticides without adsorbent were also shaken for 24 h and served as controls. The percentage of pesticide adsorbed (% Ads) was calculated as: % Ads = [(Ci - Ce)/Ci] x 100.

The HPLC system used for the determination of the initial and equilibrium pesticide concentrations was a Waters 600E chromatograph coupled to a Water 996 diode-array

detector. External calibration with four standard solutions between 0.1 and 2 mg L^{-1} was used in the calculations. Different analytical conditions, in terms of chromatographic column, mobile phase, flow rate, and detection wavelength were required to analyze each pesticide; this information is compiled in Table S1 of the Supplementary data.

2.4.2. Adsorption-desorption isotherms of mecoprop (MCPP) on SA-HEXAD and SA-HDTMA

According to the adsorption displayed by the pesticides on the organo-clays, mecoprop (MCCP) was chosen as a probe in order to get deep insight into the molecular interaction mechanism between anionic pesticides and the nanocomposites. For this purpose, adsorption and desorption isotherms of MCPP on SAz-1, SA-HEXAD and SA-HDTMA were obtained. Triplicate 20 mg of each adsorbent were placed in glass centrifuge tubes lined with screw caps. Subsequently, 8 mL of aqueous solutions of MCPP with initial concentrations ranging between 0.1 and 2 mg L^{-1} were added and the resulting suspensions were equilibrated by shaking at 20 ± 2 ºC for 24 h. After equilibration, the suspensions were centrifuged and 4 mL of the supernatant solution were removed, filtered and analyzed by HPLC to determine the equilibrium concentration (Ce) of MCPP. The amount of MCPP adsorbed, Cs (mg kg^{-1}), was calculated from the difference between the initial and equilibrium solution concentrations.

The MCPP adsorption isotherms on SA-HEXAD was fitted to the linearized form of five two-parameter models (Langmuir, Freundlich, Temkin, Flory-Huggins, and Dubinin-Radushkevich) [41] and the corresponding adsorption parameters were calculated.

Desorption isotherms were obtained immediately after adsorption from the highest initial concentration point of the adsorption isotherm (2 mg L^{-1}). The 4 mL of supernatant removed for the adsorption analysis were replaced with 4 mL of distilled water. After shaking at 20 ±

2°C for 24 h, the suspensions were centrifuged and the MCPP concentration was determined in the supernatant by HPLC. This desorption procedure was repeated three times.

2.4.3. Adsorption mechanism of MCPP on SA-HEXAD and SA-HDTMA

A separate experiment was also conducted to elucidate the mechanisms involved in the adsorption of MCPP by the tested organo-clays. The working hypothesis was to assume that if non-specific ionic interactions motivated the adsorption of MCPP on SA-HEXAD, the presence of other anions in solution would depress the adsorption of the pesticide. Thus, the influence of electrolyte ($CaCl_2$) concentration in solution on the adsorption of MCPP by SA-HEXAD and SA-HDTMA was appraised. Adsorption at single initial concentration of MCPP (1 mg L^{-1}) on the organo-clays was performed by the batch method in water, 0.01 M $CaCl_2$ and 0.1 M $CaCl_2$ as background solutions. The procedure used to determine the percentage of MCPP adsorbed was identical to that described in section 2.4.1.

3. Results and discussion

3.1. Characterization of the unmodified and modified montmorillonites

3.1.1. Elemental analysis

The C and N contents of the unmodified and modified montmorillonite samples were used to calculate the percentage of the CEC of SAz-1 compensated by organic cations. According to the elemental analysis, HDTMA readily compensated (101%) the whole CEC of SAz-1, whereas the amount of HEXAD present accounted for 85% of the CEC of the clay mineral. This may suggest some difficulties for the polymer HEXAD to be intercalated into the clay, most likely as a consequence of its larger size compared to HDTMA (Fig. S1). The amounts of organic modifier in SA-HEXAD and SA-HDTMA were in good agreement with the values reported by Celis et al. [24] for similar organo-clays.

195

196 *3.1.2. X-ray diffraction*

197 The XRD diagrams of SAz-1, SA-HEXAD and SA-HDTMA showed the classical patterns
198 of montmorillonites, where d_{001} values depended on the cation existing in the interlayer space
199 (Fig. 2). The basal spacing of the unmodified SAz-1 montmorillonite was 1.52 nm, similar to
200 the value reported in earlier studies [31,42]. The spacing of 1.52 nm is characteristic of two
201 layers of hydration water surrounding the Ca^{2+} ions in the interlayer space [2,30,43]. The
202 modification of SAz-1 with HEXAD resulted in a well-defined diffraction peak at 1.40 nm.
203 This value is in agreement with a monolayer arrangement of the organic polymer in the
204 interlayer space of the clay mineral, as previously proposed by Celis et al. [24]. The decrease in
205 the d_{001} value of SAz-1 upon modification with HEXAD indicated that the incorporation of the
206 organic cation into the clay mineral interlayer led to reduced swelling of the clay mineral
207 compared to the presence of hydrated Ca^{2+} as counter ions [24,28]. Nevertheless, the basal
208 spacing of 1.40 nm obtained for SA-HEXAD was greater than the values obtained for
209 horizontal monolayer arrangements of other alkylammonium-exchanged montmorillonites
210 [30,44–46] where ammonium groups ($-NH_2-^+$ or $-NH_3^+$) were keyed into the ditrigonal cavities
211 of the layers and established strong hydrogen bonds with the surface oxygen atoms [43,47].
212 This may reflect the steric hindrance of the $–N(CH_3)_2^+-$ groups of hexadimethrine (Fig. S1) to
213 be keyed into the ditrigonal cavities, as observed for other quaternary ammonium cations
214 [8,40,48]. On the other hand, the d_{001} value corresponding to SA-HDTMA was 2.25 nm (Fig.
215 2), which is characteristic of a paraffinic arrangement of the HDTMA cations in the interlayer
216 region in this organo-clay [31,49].

217

218 *3.1.3. FTIR study*

The FTIR technique was used to ascertain the presence of the organic modifiers in the prepared organo-clays (Fig. 3). The spectrum of SAz-1 showed bands at 3610 and 3390 cm^{-1} in the hydroxyl stretching vibration region, υ(OH), the former corresponding to the structural OH groups of montmorillonite, and the latter to O-H vibrations of hydration water. It also showed a band at 1630 cm^{-1} attributed to the O-H bending mode, δ(OH), of water molecules, and a band at 980 cm^{-1} due to the representative Si-O-Si stretching mode in clay minerals [2]. After modification of the clay mineral with the organic cations, the band at 3610 cm^{-1} remained unshifted for both organo-clays, indicating that the organic cations did not trigger significant changes on the clay layers. However, upward shifting of the bands assigned to the υ(OH) stretching and δ(OH) bending modes of hydration water were registered for both SA-HEXAD (3430 cm^{-1} and 1640 cm^{-1}) and SA-HDTMA (3410 cm^{-1} and 1640 cm^{-1}) (Fig. 3). This indicated higher freedom for water molecules in the organo-clays than that in the starting material, because polar interactions of the residual water molecules with the organic cations were weaker than those between water molecules and Ca^{2+} ions present in the pristine material. In addition, the low intensity observed for these bands was a consequence of the less hydration degree of the organo-clays compared to the unmodified mineral [24,30], which is consistent with the decrease in d_{001} value observed for SA-HEXAD compared to the starting material, SAz-1 (Fig. 2).

A remarkable feature of the FT-IR spectra was that both organo-clays exhibited bands characteristic of symmetric and antisymmetric C-H stretching vibrations, at 2950 and 2870 cm^{-1} for SA-HEXAD and 2923 and 2851 cm^{-1} for SA-HDTMA [50]. The group of bands appearing between 1490 and 1420 cm^{-1} in SA-HEXAD and between 1487 and 1416 cm^{-1} in SA-HDTMA can be assigned to C-H deformation vibrations [50]. The position of these bands at lower wavenumbers for SA-HDTMA respect to SA-HEXAD can be an indication of closer packing of the $-CH_2-$ groups, i.e. higher density of the alkylammonium chains, in the interlayer

space of SA-HDTMA, where the vibration of $–CH_2-$ groups appears to be more hindered than in SA-HEXAD.

3.1.4. N_2 adsorption isotherms: Determination of BET surface area

The N_2 adsorption isotherms for the unmodified and modified-montmorillonites samples (Fig. S2) showed the typical shape for clay materials [43,51–54]. The adsorption isotherms for all samples were type II, according to the IUPAC classification. The inflection points observed in the curves indicated the stage at which monolayer coverage is completed and multilayer adsorption begins to occur. In addition, the large nitrogen uptake observed close to saturation pressure is assigned to the presence of mesopores [43,53]. The modification of SAz-1 with HEXAD and HDTMA resulted in different BET specific surface area values (S_{BET}), which can be related to the nature of the organic cations and their arrangement on the mineral surfaces (Fig. S2). According to the N_2 isotherms, the S_{BET} decreased gradually in the following order: SAz-1 (80 $m^2 g^{-1}$) > SA-HEXAD (51 $m^2 g^{-1}$) > SA-HDTMA (11 $m^2 g^{-1}$), similar to the behavior reported by Wang et al. [54] for untreated and HDTMA-treated SAz-1 montmorillonite. The decrease in the S_{BET} for smectites upon treatment with organic cations has previously been observed by other authors [53–55], who attributed this effect to the organic cations clogging the pores and restricting the diffusion of N_2 [56]. Accordingly, the lower surface area and less hysteresis showed by SA-HDTMA compared to SA-HEXAD may reflect a more efficient surface covering and pore filling by HDTMA compared to HEXAD. It should be kept in mind that N_2 adsorption is commonly considered as a measure of the external surface area and, as such, it should not be used for total specific surface area or as an indicator of the amount of chemically accessible internal surface area. Considering preceding works, N_2 is not a suitable adsorbate for materials having pores smaller than 0.5 nm [57].

3.1.5. Zeta potential

The zeta potential (ξ) distribution curves for SAz-1, SA-HEXAD, and SA-HDTMA in water suspension are shown in Fig. 4. The zeta potential distribution curves of SAz-1 and SA-HDTMA, with maximum values at -23.8 mV and -4.6 mV, respectively, were in good agreement with results previously published by other authors [58,59]. These negative values reflect the key role of the external surfaces of the clay mineral [60]. Bate and Burns [60] pointed out that the zeta potential for organoclays became less negative for longer chains in alkylammonium-modified montmorillonite, suggesting some interactions of the organic cations within the shear plane. In contrast, several maximums, predominantly located at positives values, were observed in the zeta potential distribution curve of SA-HEXAD (Fig. 4). It is worthy to highlight that positive values of zeta potential were reported by other authors for organoclays when the amount of organic cation present exceeded the CEC of the clay [60]. Bleiman and Mishael [61] also obtained positive values of zeta potential upon montmorillonite modification with chitosan, a positively-charged polymer. Hexadimethrine is a macromolecule and, as proposed by Lagaly [62], it can be expected that its arrangement in the montmorillonite surface would be governed by the distribution of charges in both the polymer and the clay [62]. Due to the heterogeneity of the charge distribution of clay mineral surfaces, it is likely that the polymer interacted with the clay surface forming loops and/or exposing unbalanced positive charges outside the sheets (Fig. 5) in such a way that not all $-N(CH_3)_2-^+$ groups present in HEXAD directly interacted with the clay surface to compensate the layer charge of SAz-1 [62]. This would explain the positive zeta potential values observed in Fig. 4.

3.1.6. Scanning electron microscopy (SEM)

No great morphological changes were observed among samples when SAz-1, SA-HEXAD and SA-HDTMA were visualized at the micrometer scale by SEM (Fig. S3). This fact suggested either "functional" character of the nanohybrids, due to their different surface properties at the molecular scale, or that morphological differences primarily occurred at the nanometer scale, so that they could only have been seen at higher magnifications. It is well documented that the final morphology of organo-clays is conditioned by the nature and packing of the organic cation [26]. The unmodified SAz-1 montmorillonite showed aggregated and curled particles, whereas SA-HDTMA developed less aggregated morphology and flat plates and SA-HEXAD displayed an intermediate state between both (Fig. S3). It should be pointed out that for neither SA-HEXAD nor SA-HDTMA the amount of organic cation exceeded the CEC of the clay, and morphological changes at the micrometer scale have been reported mainly for organo-clays in which the amount of organic cation present exceeded the CEC of the clay mineral. In such cases, the structure became more regularly stacked [53] or montmorillonite adopted the shape of the organic modifier, as observed for SWy-2 montmorillonite modified with the cationic polymer chitosan [27].

3.2. Pesticide adsorption study on the organo-clays

3.2.1. Adsorption of pesticides on unmodified and modified montmorillonite at single initial concentration

The percentage of each pesticide adsorbed on unmodified and HEXAD- and HDTMA-modified SAz-1 montmorillonite is compiled in Table 1. It is important to note that at the pH of the equilibrated suspensions during the adsorption experiment (pH> 6), fluometuron, diuron, terbuthylazine and simazine existed as neutral species, whereas MCPP, MCPA and clopyralid (with p*K*a< 4) existed mainly as anionic species. The original SAz-1 montmorillonite displayed very little affinity for all assayed pesticides (adsorption percentage < 5%), but its

318 modification with HEXAD and HDTMA yielded organo-clays with greater affinity for selected
319 pesticides (Table 1). The adsorptive behavior of the organo-clays depended on the properties
320 of both the organic modifier and the considered pesticide. Thus, SA-HDTMA displayed high
321 affinity for all pesticides (adsorption percentage > 70%) except simazine (Table 1), most likely
322 due to its paraffinic structure which favors hydrophobic interactions with organic compounds
323 [24,31,48]. However, SA-HEXAD displayed good adsorption of anionic pesticides only (i.e.,
324 mecoprop, clopyralid, and MCPA), for which adsorption percentages ranged between 50 and
325 75%. This fact is in agreement with the maximums located at positive values of the zeta
326 potential value registered for this organo-clay (Fig. 4) and also with the hypothesis that the
327 polymer would be bound to the clay surface exposing some $-N(CH_3)_2-^+$ groups not directly
328 interacting with the clay surface (Fig. 5), because these groups would act as adsorption sites
329 for anionic pesticides. On the basis of its high adsorption on both nanohybrids, MCPP was
330 selected for subsequent experiments designed to get further insight into the mechanisms
331 governing the adsorption of anionic pesticides on SA-HEXAD and SA-HDTMA.
332
333 *3.2.2. Adsorption-desorption isotherm of MCPP on SA-HDTMA and SA-HEXAD*
334 Adsorption-desorption isotherms of MCPP on SA-HEXAD and SA-HDTMA are shown in
335 Fig. 6. Since most of the pesticide present in the solution was uptaken by SA-HDTMA, only
336 the adsorption isotherms for SA-HEXAD could be fitted to the two-parameter models
337 explored in this work (Table 2). Among the different models tested, the Freundlich equation
338 led to the best fitting of the MCPP adsorption data on SA-HEXAD (R^2 = 0.999).
339 The different adsorption behavior of MCPP on SA-HEXAD and SA-HDTMA was probably
340 due to the distinct arrangement of the organic modifiers in the interlayer space of the clay [11].
341 Based on its shape, and supported by the obtained Freundlich N_f value of 1.22 ± 0.02 (Table
342 S2), the adsorption isotherm of MCPP on SA-HEXAD was S-type according to the Giles et al.

343 [63] classification, similar to the isotherms obtained for the pesticide MCPA on the same
344 organo-clay [23,24]. S-type isotherms are often related to competition between water
345 molecules or ionic species in solution and the organic compound for adsorption sites and/or
346 strong intermolecular interaction within the adsorbed layer of organic compound [63,64].
347 Hence, these results, together with zeta potential measurements (Fig. 4), strongly indicate that
348 hexadimethrine polymer provided excess of positive charge which would contribute to the
349 affinity displayed by SA-HEXAD for MCPP. The pesticide would be adsorbed by ionic forces,
350 and intermolecular attraction probably occurred between the hydrophobic moieties (phenyl
351 rings) of adsorbed MCPP species to result in the observed S-type isotherm behavior.
352 As mentioned above, the high adsorption of MCPP exhibited by SA-HDTMA can be related
353 to hydrophobic interactions between the pesticide and the adsorbent, allowed by the paraffinic
354 structure of the interlayer of this organo-clay [11,45]. As previously proposed by Hermosín
355 and Cornejo [36] for the anionic pesticide 2,4-D, the adsorption could have also involved polar
356 interactions between the ammonium groups of the alkylammonium and the carboxylic group of
357 MCPP.
358 It is meaningful that, according to the desorption isotherm, MCPP showed some resistance
359 to be desorbed from SA-HEXAD (Fig. 6). This circumstance can also be considered as an
360 indication that the adsorption of this pesticide was governed by ionic forces, as formerly
361 reported for the desorption of other anionic pesticides from organo-clays where water was
362 used as desorbing solution [13,27,35]. The desorption isotherm of MCPP from SA-HDTMA
363 was poorly defined as a consequence of the great adsorption capacity of this organo-clay and
364 the very low pesticide concentration remaining in solution after adsorption.
365
366 *3.2.3. Confirming the adsorption mechanism of the pesticide MCPP on SA-HEXAD and SA-*
367 *HDTMA*

368 To confirm the above-proposed adsorption mechanisms, the extent of MCPP adsorption on
369 SA-HEXAD and SA-HDTMA at different background electrolyte ($CaCl_2$) concentrations was
370 measured (Fig. 7). Our hypothesis was that if non-specific ionic interactions governed the
371 adsorption of MCPP on SA-HEXAD and hydrophobic interactions governed its adsorption on
372 SA-HDTMA, then high concentrations of a competing anion (Cl^-) would highly depress
373 adsorption of MCPP on SA-HEXAD but not on SA-HDTMA. As expected, the adsorption of
374 MCPP on SA-HEXAD was suppressed in 0.01 and 0.1 M $CaCl_2$ (Fig. 7), whereas an almost
375 negligible effect was observed for SA-HDTMA. Since the adsorption of MCPP was reduced,
376 the formation of Ca-MCPP complexes can be ruled out as a consequence of the presence of
377 $CaCl_2$, as it was reported for the adsorption of this pesticide on α-alumina and calcite [65]. In
378 summary, the striking differences found in the adsorption behavior of SA-HEXAD and SA-
379 HDTMA can be explained by different adsorption driving forces resulting from the structure of
380 each organo-clay. Electrostatic interactions of anionic pesticides, such as MCPP, with
381 positively charged sites at the surface, i.e. $-N(CH_3)_2^+-$ groups not directly involved in the
382 interaction with the clay, is proposed for SA-HEXAD. In contrast, hydrophobic interactions
383 with the hydrophobic environment associated to the paraffinic structure of SA-HDTMA should
384 be the main mechanism governing the adsorption of both neutral and anionic pesticides by this
385 organo-clay. Nevertheless, polar/ionic interactions could have also slightly contributed to the
386 adsorption of the anionic pesticides on SA-HDTMA, as indicated by the slight decrease in
387 adsorption of MCPP observed in Fig. 7 at higher $CaCl_2$ concentration [13,66].
388
389 **4. Conclusions**
390 The study developed in this work shows that the cationic polymer hexadimethrine readily
391 intercalates into SAz-1 Arizona montmorillonite with arrangement of the polycation in
392 monolayers to yield a d_{001} value of 1.4 nm. The polymer also partially covers the external

393 surface of the clay exposing some of their $-N(CH_3)_2-^+$ groups outside the interlayers of SAz-1,
394 thus providing the resultant organo-clay with anion exchange properties. Comparative
395 adsorption studies with the traditional HDTMA-modified Arizona montmorillonite (SA-
396 HDTMA) showed that the extent of adsorption of pesticides on both organo-clays was
397 conditioned by the arrangement of the organic cation on the clay surfaces. The paraffinic
398 structure of SA-HDTMA led to high adsorption of all tested pesticides, mainly by pesticide-
399 adsorbent hydrophobic interactions. In contrast, SA-HEXAD showed good adsorption of
400 anionic pesticides only, with evidence that the driving forces for adsorption were ionic
401 interactions. Therefore, we obtained a new nanocomposite based on hexadimethrine polymer
402 modified-montmorillonite with selective affinity for anionic pesticides, which could be
403 potentially useful as an adsorbent in applications such as the removal of pesticides from
404 contaminated water, their immobilization in soil, or the preparation of slow release
405 formulations. However, on the basis of the expected desorption of the adsorbed pesticide in
406 the presence of saline solutions, we believe that the adsorbent could be particularly useful in
407 the preparation of clay-based formulations of anionic pesticides to control their release once
408 incorporated into the environment.
409

410 **Acknowledgments**

411 This work has been financed the Spanish Ministry of Economy and Competitiveness
412 (MINECO Project AGL2011-23779) and Junta de Andalucía (JA Projects P07-AGR-03077
413 and P11-AGR-7400). B. Gámiz also thanks Junta de Andalucía for her postdoc-contract linked
414 to Project P07-AGR-03077.
415

416 **References**

[1] F. Bergaya, G. Lagaly, General Introduction: Clays, Clay Minerals, and Clay Science, in: F. Bergaya, B. Theng, G. Lagaly (Eds.), Handb. Clay Sci., Elsevier, Amsterdam, 2006: pp. 1–18.

[2] C.T. Johnston, Probing the nanoscale architecture of clay minerals, Clay Miner. 45 (2010) 245–279.

[3] J. Cornejo, R. Celis, I. Pavlovic, M.A. Ulibarri, Interactions of pesticides with clays and layered double hydroxides: a review, Clay Miner. 43 (2008) 155–175.

[4] D.H. Park, S. Hwang, J.M. Oh, J.H. Yang, J.H. Choy, Polymer–inorganic supramolecular nanohybrids for red, white, green, and blue applications, Prog. Polym. Sci. 38 (2013) 1442–1486.

[5] D. Manikandan, R.V. Mangalaraja, R. Siddheswaran, R.E. Avila, S. Ananthakumar, Fabrication of nanostructured clay–carbon nanotube hybrid nanofiller by chemical vapour deposition, Appl. Surf. Sci. 258 (2012) 4460–4466.

[6] Z. Gu, M. Gao, Z. Luo, L. Lu, Y. Ye, Y. Liu, Bis-pyridinium dibromides modified organo-bentonite for the removal of aniline from wastewater: A positive role of π–π polar interaction, Appl. Surf. Sci. 290 (2014) 107–115.

[7] S.A. Boyd, C.T. Johnston, D.A. Laird, B.J. Teppen, Comprehensive study of organic contaminant adsorption by clays: methodologies, mechanisms, and environmental implications, in: B. Xing, N. Senesi, P.M. Huang (Eds.), Biophys. Process. Anthropog. Org. Compd. Environ. Syst., John Wiley & Sons, Inc, 2011: pp. 51–71.

[8] W.F. Jaynes, G.F. Vance, BTEX sorption by organo-clays: cosorptive enhancement and equivalence of interlayer complexes, Soil Sci. Soc. Am. J. 60 (1996) 1742–1749..

[9] G. Lagaly, Pesticide–clay interactions and formulations, Appl. Clay Sci. 18 (2001) 205–209.

[10] M. Mortland, Clay-organic interactions, Adv. Agron. 23 (1970) 75–117.

[11] S.A. Boyd, S. Shaobai, J.F. Lee, M. Mortland, Pentachlorophenol sorption by organo-clays, Clays Clay Miner. 36 (1988) 125–130.

[12] L. Groisman, C. Rav-Acha, Z. Gerstl, U. Mingelgrin, Sorption of organic compounds of varying hydrophobicities from water and industrial wastewater by long- and short-chain organoclays, Appl. Clay Sci. 24 (2004) 159–166.

[13] M. Hermosin, J. Cornejo, Removing 2,4-D from water by organo-clays, Chemosphere. 24 (1992) 1493–1503.

[14] M. Mortland, S. Shaobai, S.A. Boyd, Clay-organic complexes as adsorbents for phenol and chlorophenols, Clays Clay Miner. 34 (1986) 581–585.

[15] S. Nir, Y. El-Nahhal, T. Undabeytia, G. Rytwo, T. Polubesova, Y. Mishael, U. Rabinovitz, R. Rubin, Clays and pesticides, in: F. Bergaya, B. Theng, G. Lagaly (Eds.), Handb. Clay Sci., Elsevier, Amsterdam, 2006: pp. 677–691.

454 [16] B. Sarkar, Y. Xi, M. Megharaj, G. Krishanamurti, M. Bowman, H. Rose, R. Naidu,
455 Bioreactive Organoclay : A New Technology for Environmental Remediation, Crit. Rev.
456 Environ. Sci. Technol. (2012) 37–41.

457 [17] R. Celis, W.C. Koskinen, M. Hermosín, M.A. Ulibarri, J. Cornejo, Triadimefon
458 interactions with organoclays and organohydrotalcites, Soil Sci. Soc. Am. J. 64 (2000)
459 840–847.

460 [18] B. Gámiz, R. Celis, M.C. Hermosín, J. Cornejo, Organoclays as soil amendments to
461 increase the efficacy and reduce the environmental impact of the herbicide fluometuron
462 in agricultural soils, J. Agric. Food Chem. 58 (2010) 7893–7901.

463 [19] C. Trigo, R. Celis, M.C. Hermosín, J. Cornejo, Organoclay-based formulations to
464 reduce the environmental impact of the herbicide diuron in olive groves, Soil Sci. Soc.
465 Am. J. 73 (2009) 1652–1657.

466 [20] R. Celis, W.C. Koskinen, A.M. Cecchi, G.A. Bresnahan, M.J. Carrisoza, M.A. Ulibarri,
467 I. Pavlovic, M.C. Hermosín, Sorption of the ionizable pesticide imazamox by organo-
468 clays and organohydrotalcites, J. Environ. Sci. Heal. Part B. 34 (1999) 929–941.

469 [21] M.J. Carrizosa, W.C. Koskinen, M.C. Hermosín, Interactions of acidic herbicides
470 bentazon and dicamba with organoclays, Soil Sci. Soc. Am. J. 68 (2004) 1863–1866.

471 [22] R. Celis, M.C. Hermosín, L. Cornejo, M.J. Carrizosa, J. Cornejo, Clay-herbicide
472 complexes to retard picloram leaching in soil, Int. J. Environ. Anal. Chem. 82 (2002)
473 503–517.

474 [23] A. Cabrera, L. Cox, K.A. Spokas, R. Celis, M.C. Hermosín, J. Cornejo, W.C. Koskinen,
475 Comparative sorption and leaching study of the herbicides fluometuron and 4-chloro-2-
476 methylphenoxyacetic acid (MCPA) in a soil amended with biochars and other sorbents,
477 J. Agric. Food Chem. 59 (2011) 12550–12560.

478 [24] R. Celis, C. Trigo, G. Facenda, M.C. Hermosín, J. Cornejo, Selective modification of
479 clay minerals for the adsorption of herbicides widely used in olive groves, J. Agric. Food
480 Chem. 55 (2007) 6650–6658.

481 [25] J. Nye, W. Guerin, S.A. Boyd, Heterotrophic activity of microorganisms in soils treated
482 with quaternary ammonium compounds, Environ. Sci. Technol. 28 (1994) 944–951.

483 [26] B. Sarkar, M. Megharaj, Y. Xi, G.S.R. Krishnamurti, R. Naidu, Sorption of quaternary
484 ammonium compounds in soils: implications to the soil microbial activities, J. Hazard.
485 Mater. 184 (2010) 448–456.

486 [27] R. Celis, M.A. Adelino, M.C. Hermosín, J. Cornejo, Montmorillonite-chitosan
487 bionanocomposites as adsorbents of the herbicide clopyralid in aqueous solution and
488 soil/water suspensions, J. Hazard. Mater. 209-210 (2012) 67–76.

489 [28] M. Cruz-Guzmán, R. Celis, M.C. Hermosín, J. Cornejo, Adsorption of the herbicide
490 simazine by montmorillonite modified with natural organic cations, Environ. Sci.
491 Technol. 38 (2004) 180–186.

[29] B. Gámiz, R. Celis, L. Cox, M.C. Hermosín, J. Cornejo, Effect of olive-mill waste addition to soil on sorption, persistence, and mobility of herbicides used in Mediterranean olive groves, Sci. Total Environ. 429 (2012) 292–299.

[30] B. Gámiz, R. Celis, M.C. Hermosín, J. Cornejo, C.T. Johnston, Preparation and characterization of spermine-exchanged montmorillonite and interaction with the herbicide fluometuron, Appl. Clay Sci. 58 (2012) 8–15.

[31] W.F. Jaynes, S.A. Boyd, Clay mineral type and organic compound sorption by hexadecyltrimethlammonium-exchanged clays, Soil Sci. Soc. Am. J. 55 (1991) 43–48.

[32] M.G. Roberts, H. Li, B.J. Teppen, S.A. Boyd, Sorption of nitroaromatics by ammonium- and organic ammonium-exchanged smectite: shifts from adsorption/complexation to a partition-dominated process, Clays Clay Miner. 54 (2006) 426–434.

[33] M.E. Parolo, G.R. Pettinari, T.B. Musso, M.P. Sánchez-Izquierdo, L.G. Fernández, Characterization of organo-modified bentonite sorbents: The effect of modification conditions on adsorption performance, Appl. Surf. Sci. 320 (2014) 356–363.

[34] M.J. Carrizosa, M.C. Hermosín, W.C. Koskinen, J. Cornejo, Use of organosmectites to reduce leaching losses of acidic herbicides, Soil Sci. Soc. Am. J. (2003) 511–517.

[35] M. Cruz-Guzmán, R. Celis, M.C. Hermosín, W.C. Koskinen, J. Cornejo, Adsorption of pesticides from water by functionalized organobentonites, J. Agric. Food Chem. 53 (2005) 7502–7511.

[36] M. Hermosín, J. Cornejo, Binding mechanism of 2,4-D from water by organo-clays, J. Environ. Qual. 22 (1993) 325–331.

[37] C. Wang, Y. Ding, B.J. Teppen, S.A. Boyd, C. Song, H. Li, Role of interlayer hydration in lincomycin sorption by smectite clays, Environ. Sci. Technol. 43 (2009) 6171–6176.

[38] M. Kikura, M. Lee, J. Levy, Heparin neutralization with methylene blue, hexadimethrine, or vancomycin after cardiopulmonary bypass, Anesth Analg. 83 (1996) 223–227.

[39] N.H. Wang, S.L. Lo, Preparation, characterization and adsorption performance of cetyltrimethylammonium modified birnessite, Appl. Surf. Sci. 299 (2014) 123–130.

[40] R. Celis, M.C. Hermosín, M.J. Carrizosa, J. Cornejo, Inorganic and organic clays as carriers for controlled release of the herbicide hexazinone, J. Agric. Food Chem. 50 (2002) 2324–2330.

[41] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, 156 (2010) 2–10.

[42] C.J. Wang, Z. Li, W.T. Jiang, J.S. Jean, C.C. Liu, Cation exchange interaction between antibiotic ciprofloxacin and montmorillonite, J. Hazard. Mater. 183 (2010) 309–314.

[43] M. Gautier, F. Muller, L. Le Forestier, J.M. Beny, R. Guegan, NH_4-smectite: Characterization, hydration properties and hydro mechanical behaviour, Appl. Clay Sci. 49 (2010) 247–254.

[44] J.W. Jordan, Organophilic bentonites. I. Swelling in organic liquids, J. Phys. Chem. 53 (1949) 294–306.

[45] G. Lagaly, Characterization of clays by organic compounds, Clay Miner. 16 (1981) 1–21.

[46] J.M. Serratosa, J. Rausell-Colom, J. Sanz, Charge density and its distribution in phyllosilicates: Effect on the arrangement and reactivity o adsorbed species, J. Mol. Catal. 27 (1984) 225–234.

[47] C.T. Johnston, E. Tombácz, Surface chemistry of soil minerals, in: J. Dixon, D. Schulze (Eds.), Soil Mineral. with Environ. Appl., Book Serie, SSSA, Madison, 2002: pp. 37–67.

[48] J. Brixie, S. Boyd, Treatment of contaminated soils with organoclays to reduce leachable pentachlorophenol, J. Environ. Qual. 23 (1994) 1283–1290.

[49] G. Lagaly, Layer charge heterogeneity in vermiculites, Clays Clay Miner. 30 (1982) 215–222.

[50] D.A. Myrzakozha, T. Hasegawa, J. Nishijo, T. Imae, An infrared study of molecular orientation and structure in one-layer Langmuir - Blodgett films of octadecyldimethylamine oxide and dioctadecyldimethylammonium chloride : Dependence of the structures of the Langmuir - Blodgett films on substrates, aging, and pH of water subphase, Langmuir. 15 (1999) 6890–6896.

[51] R.M. Barrer, D.M. MacLeod, Intercalation and sorption by montmorillonite, Trans. Faraday Soc. 50 (1954) 980–989.

[52] S.K. Gregg SJ, Adsorption surface area and porosity, 2nd ed., Academic Press, London, 1982.

[53] H. He, Q. Zhou, W.N. Martens, T.J. Kloprogge, P. Yuan, Y. Xi, J. Zhu, R.L. Frost, Microstructure of $HDTMA^+$-modified montmorillonite and its influence on sorption characteristics, Clays Clay Miner. 54 (2006) 689–696.

[54] C.C. Wang, L.C. Juang, C.K. Lee, T.C. Hsu, J.F. Lee, H.P. Chao, Effects of exchanged surfactant cations on the pore structure and adsorption characteristics of montmorillonite, J. Colloid Interface Sci. 280 (2004) 27–35.

[55] Y. Park, G.A. Ayoko, R.L. Frost, Characterisation of organoclays and adsorption of p-nitrophenol: environmental application, J. Colloid Interface Sci. 360 (2011) 440–56.

[56] H. He, R.L. Frost, T. Bostrom, P. Yuan, L. Duong, D. Yang, Y. Xi, J.T. Kloprogge, Changes in the morphology of organoclays with $HDTMA^+$ surfactant loading, Appl. Clay Sci. 31 (2006) 262–271.

[57] H. de Jonge, M. Mittelmeijer-Hazeleger, Adsorption of CO_2 and N_2 on soil organic matter: Nature of porosity, surface area, and diffusion mechanisms, Environ. Sci. Technol. 30 (1996) 408–413.

[58] E. Tombácz, M. Szekeres, Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite, Appl. Clay Sci. 34 (2006) 105–124.

[59] P. Zarzycki, P. Szabelski, W. Piasecki, Modelling of ζ-potential of the montmorillonite/electrolyte solution interface, Appl. Surf. Sci. 253 (2007) 5791–5796.

[60] B. Bate, S.E. Burns, Effect of total organic carbon content and structure on the electrokinetic behavior of organoclay suspensions, J. Colloid Interface Sci. 343 (2010) 58–64.

[61] N. Bleiman, Y.G. Mishael, Selenium removal from drinking water by adsorption to chitosan-clay composites and oxides: batch and columns tests, J. Hazard. Mater. 183 (2010) 590–595.

[62] G. Lagaly, Inorganic Layer Compounds, Naturwissenenschaften. 68 (1981) 82–88.

[63] C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, Studies in Adsorption. Part XI. A System of classification of solution adsorption isotherms, and its use un diagnosis of adsorption mechanism in measurement of specific surface area in solids, J. Chem. Soc. 846 (1960) 3973–3993.

[64] R. Celis, M.C. Hermosin, L. Cox, J. Cornejo, Sorption of 2, 4-dichlorophenoxyacetic acid by model particles simulating naturally occurring soil colloids, Environ. Sci. Technol. 33 (1999) 1200–1206.

[65] L. Clausen, I. Fabricius, L. Madsen, Adsorption of pesticides onto quartz, calcite, kaolinite, and alpha-alumina, J. Environ. Qual. 30 (2000) 846–57.

[66] M.J. Carrizosa, W.C. Koskinen, M.C. Hermosin, J. Cornejo, Dicamba adsorption–desorption on organoclays, Appl. Clay Sci. 18 (2001) 223–231.

FIGURE CAPTIONS

Fig. 1. Structure of the pesticides used in this work.

Fig. 2. X-ray diffraction patterns of SAz-1, SA-HEXAD and SA-HDTMA.

Fig. 3. Fourier-transform infrared spectra of SAz-1, SA-HEXAD and SA-HDTMA.

Fig. 4. Zeta potential distribution curves for SAz-1, SA-HEXAD and SA-HDTMA.

Fig. 5. Schematic representation of the arrangement of HEXAD on SAz-1 bound to the surface forming loops and leaving positive charges on the external surface of the clay. Adapted from Lagaly [62].

Fig. 6. Adsorption-desorption isotherms of MCPP on SA-HEXAD and SA-HDTMA.

Fig. 7. Effect of salt concentration on the adsorption of MCPP by SA-HEXAD and SA-HDTMA.

612 **Table 1**

613 Percentage of pesticide adsorbed on SAz-1, SA-HEXAD and SA-HDTMA

Pesticide	SAz-1	SA-HEXAD	SA-HDTMA
Fluometuron	< 5	< 5	90 ±1[a]
Diuron	< 5	< 5	95 ± 1
Terbuthylazine	< 5	< 5	77 ± 1
Simazine	< 5	< 5	28 ± 1
Mecoprop (MCPP)	< 5	70 ± 2	95 ± 1
MCPA	< 5	54 ± 3	94 ± 1
Clopyralid	< 5	75 ± 3	84 ± 1

614 [a] value ± standard error

615

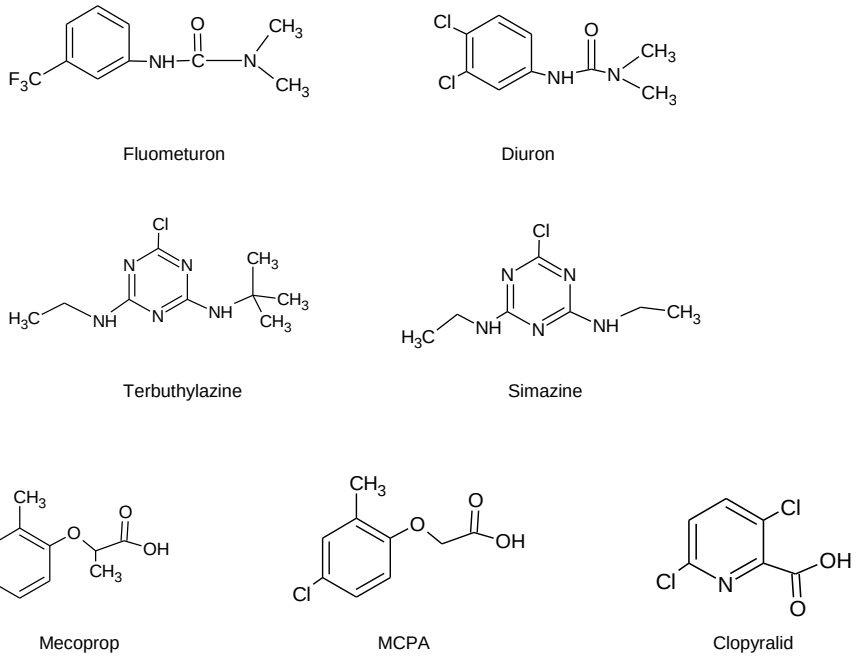
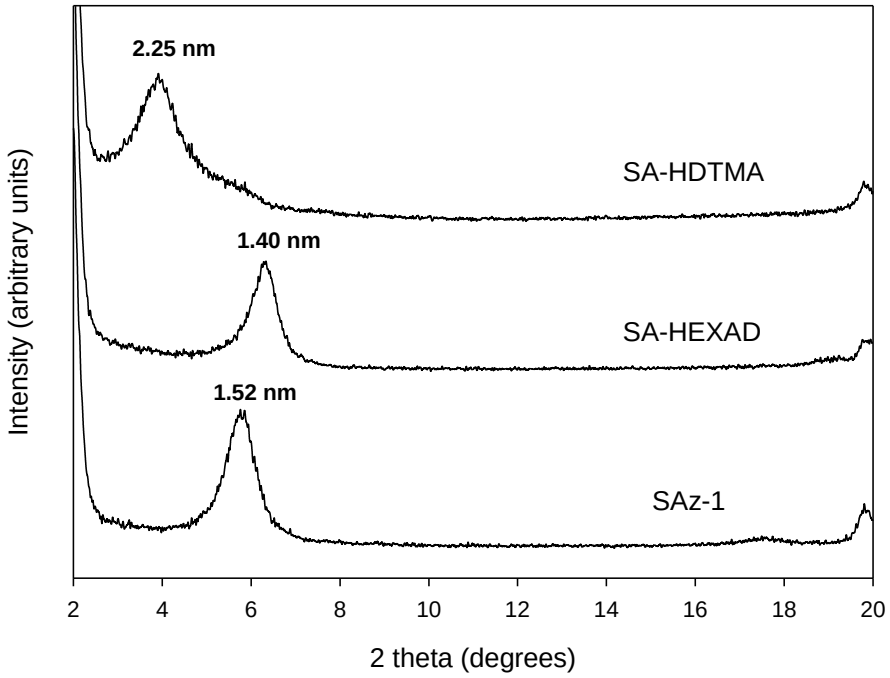


Fig. 1. Structure of the pesticides used in this work.

630



631

632

633

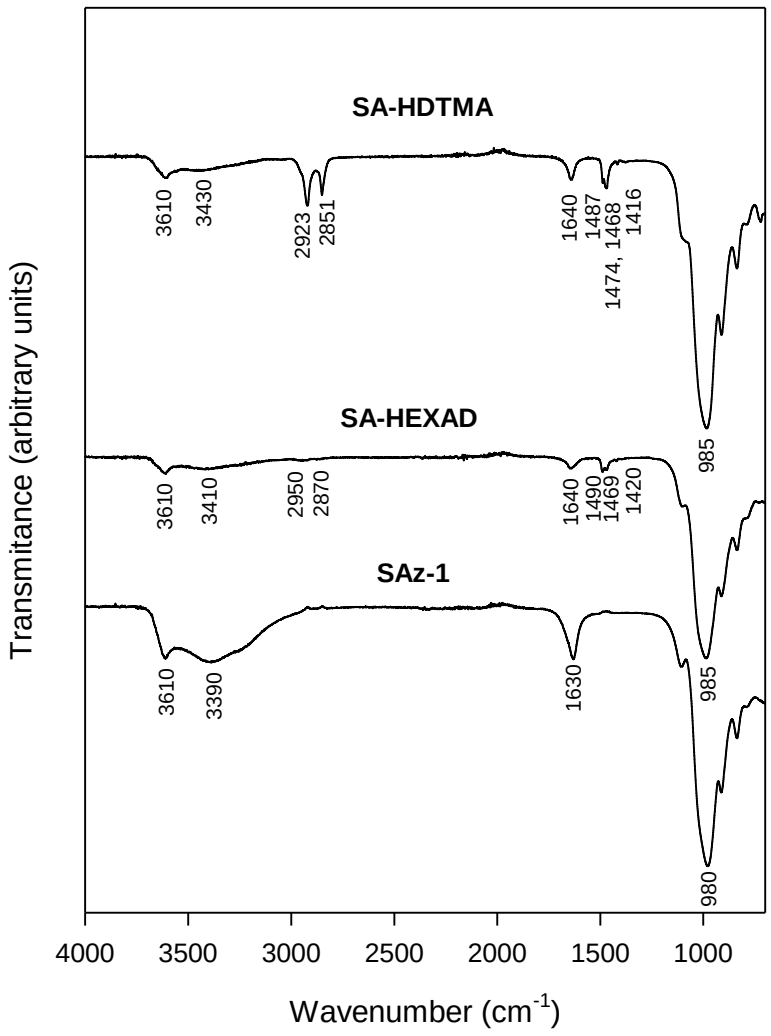
634 **Fig. 2**. X-ray diffraction patterns of SAz-1, SA-HEXAD and SA-HDTMA.

635

636

637

638



639

640

641

642 **Fig. 3**. Fourier-transform infrared spectra of SAz-1, SA-HEXAD and SA-HDTMA.

643

644

645

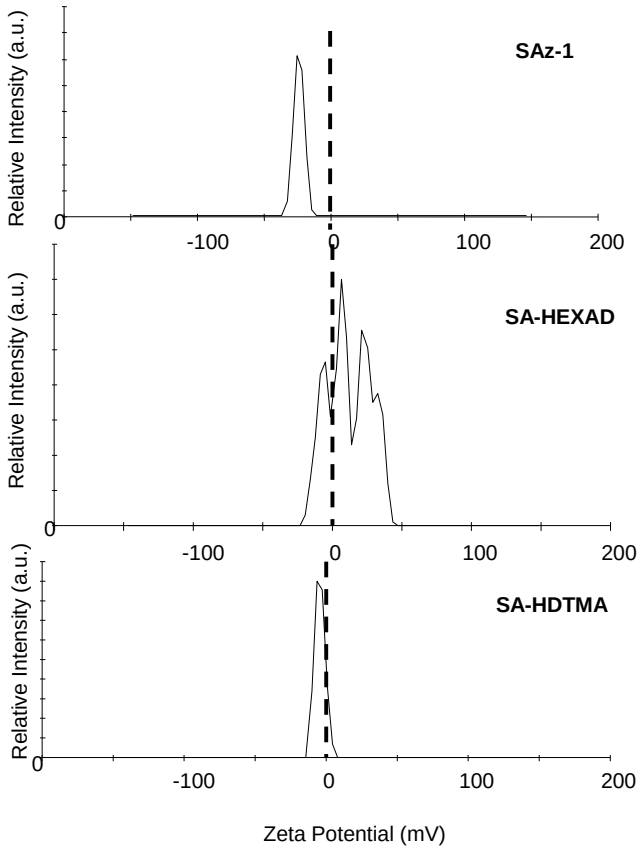


Fig. 4. Zeta potential distribution curves for SAz-1, SA-HEXAD and SA-HDTMA.

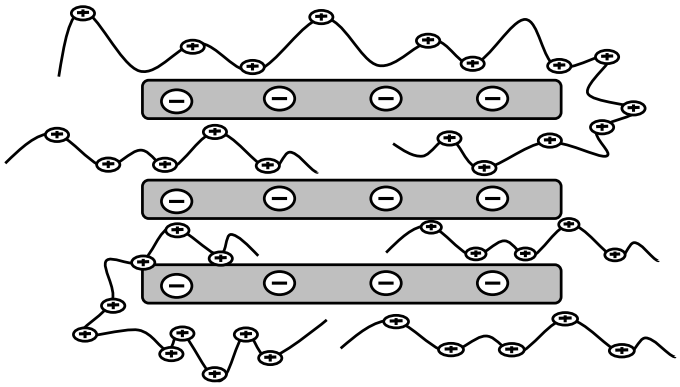
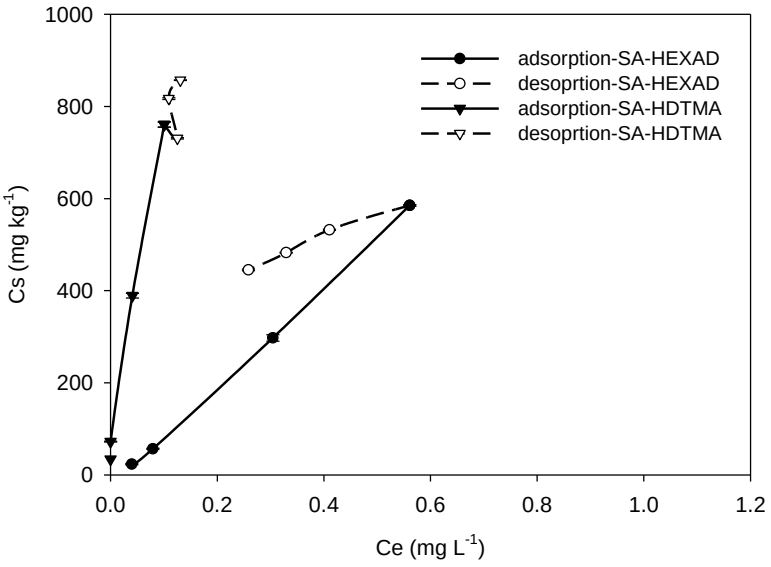


Figure 5. Schematic representation of the arrangement of HEXAD on SAz-1 bound to the surface forming loops and leaving positive charges on the external surface of the clay. Adapted from Lagaly [62].

664



665

666

667

668 **Fig. 6**. Adsorption-desorption isotherms of MCPP on SA-HEXAD and SA-HDTMA.

669

670

671

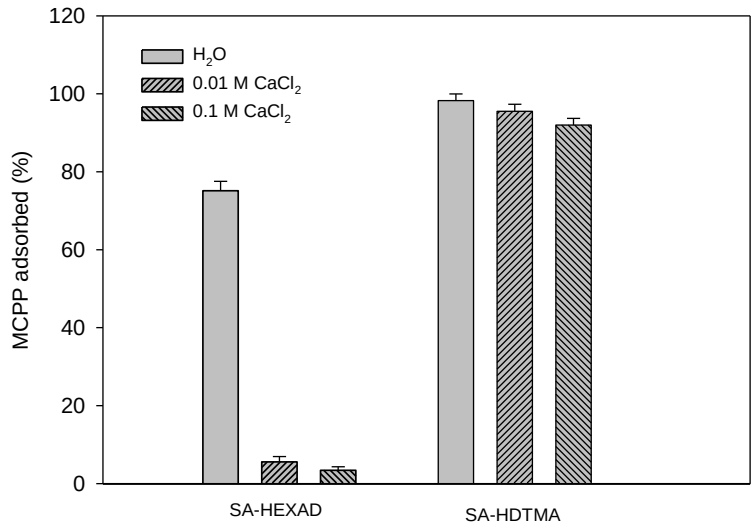


Fig. 7. Effect of salt concentration on the adsorption of MCPP by SA-HEXAD and SA-HDTMA.

Supplementary Data

Hexadimethrine-montmorillonite nanocomposite: characterization and application as a pesticide adsorbent

B. Gámiz*, M.C. Hermosín, J. Cornejo, R. Celis

Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC, Avenida Reina Mercedes 10, P.O. Box 1052, 41080 Sevilla, Spain

*bgamiz@irnase.csic.es

Table S1

Chromatographic conditions used for the analysis of the pesticides by HPLC[a].

Pesticide	Mobile phase[b]	Flow rate (mL/min)	Detection wavelength (nm)
Fluometuron	ACN:H_2O (40:60)	1	243
Diuron	ACN:H_2O (40:60)	1	250
Terbuthylazine	ACN:H_2O (50:50)	1	220
Simazine	ACN:H_2O (30:70)	1	230
Mecoprop (MCPP)	MeOH:H_3PO_4 dil. (70:30)	1	226
MCPA	MeOH:H_3PO_4 dil. (60:40)	1	230
Clopyralid	ACN:H_3PO_4 dil. (10:90)	0.7	222

[a] In all cases, except for mecoprop, the chromatographic column was a Waters Nova-Pack C18 column of 150 mm length × 3.9 mm internal diameter. For MCPP the column was a Supelcosil LC-18-DB of 150 mm length x 4.6 mm internal diameter. The sample injection volume was 25 µL.

[b] ACN: acetonitrile; MeOH: methanol; H_3PO_4 dil.: diluted o-phosphoric acid (pH= 2).

760

761 **Table S2**

762 Linear forms and parameters of the isotherm models used in this work for adsorption of MCPP

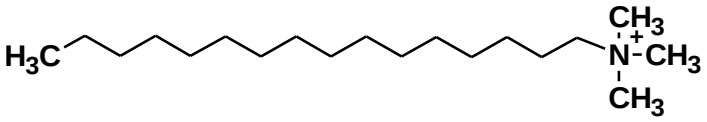
763 on SA-HEXAD.

Models	Linear form	Parameters	R^2
Freundlich[a]	$\log Cs = \log K_f + N_f log Ce$	N_f = 1.22 K_f = 1224	0.999
Flory-Huggins[b]	$\log \frac{\theta}{Co} = \log K_{FH} + n_{FH} \log(1-\theta)$	K_{FH} = 4673 n_{FH} = 7.27	0.990
Dubinin-Radushkevich[c]	$\ln Cs = \ln q_s - K_{ad}\varepsilon^2$	q_s = 676 K_{ad} = 5.59 10^{-8}	0.980
Temkin[d]	$Cs = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln Ce$	A_T = 21.40 b_T = 11.94	0.906
Langmuir[e]	$\frac{Ce}{Cs} = \frac{1}{CmL} + \frac{Ce}{Cm}$	C_m = -780 L = -0.809	0.797

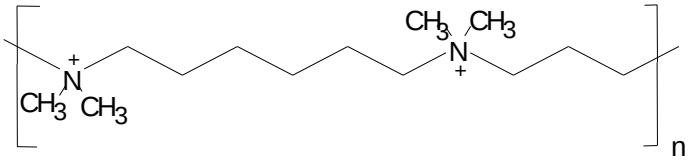
764 [a] Ce: equilibrium concentration (mg L^{-1}); Cs: amount adsorbed (mg kg^{-1}); K_f (mg^{1-Nf} kg^{-1} L^{Nf}) and N_f are
765 the Freundlich parameters
766 [b] $\theta = (1-C_e/C_o)$; C_o: initial concentration (mg L^{-1}); K_{FH}: Flory-Huggins equilibrium constant (L mg^{-1});
767 n_{FH}: Flory-Huggins model exponent
768 [c] q_s is the theoretical adsorption capacity of the adsorbent (mg kg^{-1}); K_{ad}: constant related to the
769 adsorption energy (mol^2 J^{-2}); $\varepsilon = RT \ln [1+(1/Ce)]$, R =8.314 (J mol^{-1} K^{-1}) and T temperature (K)
770 [d] A_T :Temkin constant (L kg^{-1}); b_T: Temkin constant related to heat of adsorption (J mol^{-1})
771 [e] Cm: adsorbent monolayer capacity (mg kg^{-1}); L: Langmuir adsorption constant (L mg^{-1})
772

773

774



Hexadecyltrimethylammonium (HDTMA)



Hexadimethrine (HEXAD)

Fig. S1. Structure of hexadecyltrimethylammonium (HDTMA) and the polymer hexadimethrine (HEXAD).

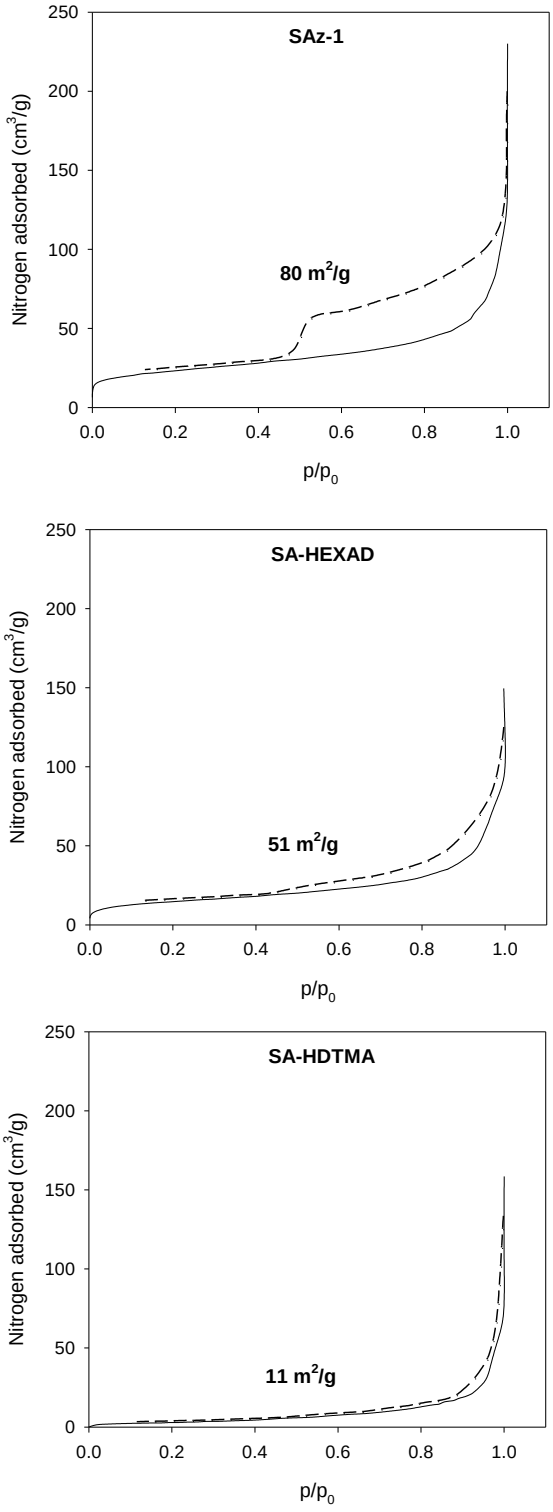


Fig. S2. N_2 adsorption isotherms and BET specific surface area of SAz-1, SA-HEXAD and SA-HDTMA.

822

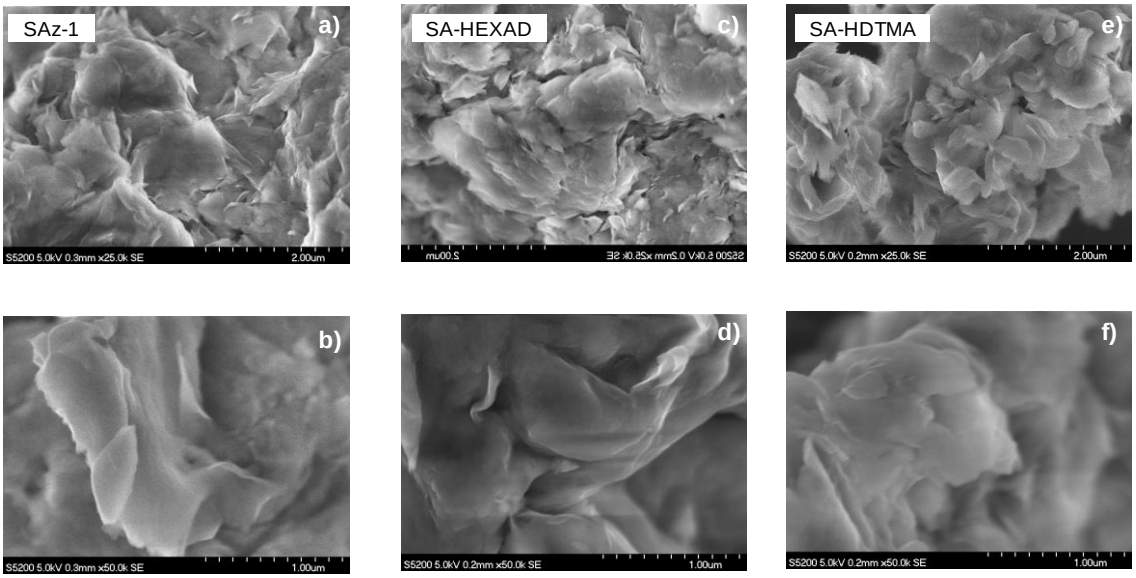


Fig. S3. SEM micrographs of SAz-1 (a and b), SA-HEXAD (c and d), and SA-HDTMA (e and f).